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<p>The relationship between the interface of glass fabric/resin and the resultant composite Mode I delamination fracture toughness in a glass fabric laminate was investigated using a double cantilever beam (DCB) specimen. The treatment of glass with silane coupling agents has been shown to improve the mechanical properties of the composite as a function of the type of coupling agent used. Two silane coupling agents, γ-aminopropyltriethoxysilane (APS) and γ-aminobutyltriethoxysilane (ABS) were used. These have similar chemistry, but differ in mobility (molecular motion). Either coupling agent improved the interfacial properties. The critical energy release rate, G_{1c}, of APS treated composites was higher than that of ABS treated composites. Thus we conclude that bulk structural properties are a function of the microscopic interfacial properties, including the dynamics of the coupling agent layer.</p>		
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Interface Mobility and Its Effect on Interlaminar
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INTRODUCTION

Laminates based on glass fabrics are used in a variety of structural applications for reinforcement. The final properties of the laminates are influenced by the properties of their constituents and structures. In addition, the properties of the interfacial regions are also very important. It is difficult to separate the contribution of each phase and interface to composite behavior. This is particularly true with the organic interphase since their molecular level behavior can be influenced by chemical or physical interactions with inorganic surfaces.

It is possible to alter the nature of the interface between dissimilar materials. One way to achieve this is through the use of coupling agents[1]. Silane coupling agents can act as a bridge between, for example, the glass fibers and the matrix. They are also used to improve the adhesion between the two constituents in a polymer composite. A significant amount of work, based on various techniques, has been done to elucidate the structure of aminosilanes in solution and on substrates[2-4]. The majority of these studies have focused on the structure of the coupling agents at or near the surface.

In addition to structure, knowledge of the molecular motion of the coupling agents may provide a better understanding of their behavior and their relationship to the physical properties of composites. Since molecular motion may vary from system to system, some consideration of the interface mobility is appropriate in the understanding of the composite properties. The focus of the present work is to determine the role that the mobility of the coupling agents play in the physical properties of composites. To do this we have chosen to compare the physical properties of composites with two similar coupling agents of different mobility. The two used are γ -aminopropyltriethoxysilane (APS) and γ -aminobutyltriethoxysilane (ABS) which have

similar structure and chemistry, but differ in their mobility in multilayer applications[5]. ABS is significantly more mobile than APS in multilayers.

One of the mechanical properties used in our comparison of two different silane coupling agents in treated composites, is interlaminar fracture toughness. A major concern in structural materials is resistance to delamination, and toughness in this mode is frequently assessed by using a double cantilever beam (DCB) specimen. Several recent papers have reported the use of composite DCB specimens to characterize mode I delamination fracture toughness[6-9]. The interlaminar fracture toughness of the treated-glass composites were measured and compared with those of untreated composites.

EXPERIMENTAL

Materials. The heat-cleaned E-glass fiber fabrics were made by Owens-Corning Fiberglas. Nominal 13 μm diameter glass fiber was used in this work. γ -aminopropyltriethoxysilane (APS) was purchased from Huls America (Piscatway, N.J.) and used as received. γ -aminobutyltriethoxysilane (ABS) was prepared by the hydrogenation of cyanopropyltriethoxysilane (CPS) under a pressure of about 100 psi in the presence of Raney nickel catalyst [10]. The product was then vacuum distilled at 30 mmHg and 85 $^{\circ}\text{C}$. The epoxy resin, diglycidylether of bisphenol A (DGEBA) and curing agent, diethylenetriamine (DETA), were obtained from Dow Chemical (labelled as DER331 and DEH20, respectively) and used as received.

Preparation. A 2% solution of the coupling agent was hydrolyzed in acetone/distilled water (10/1) for 24 hrs. The glass fabrics which were cut into 6 by 6 square inch pieces then immersed into the this solution for 24 hrs at room temperature. The treated glass fabrics were washed several times with distilled water and then dried in vacuum oven at 110 $^{\circ}\text{C}$ for half an hour.

The epoxy/hardener (10:1) was well stirred for several minutes, laminates were obtained by hand lay-up with 16-24 treated or untreated glass fabric layers in a 6"x 6" aluminum mold which was cured in a hot press at 115 $^{\circ}\text{C}$ for 30 min with a pressure about 1000 psi. To ensure complete chemical reaction, the laminates were further postcured at 140 $^{\circ}\text{C}$ for 1 hour. The laminates were then cooled slowly to reduce the residual stresses inside.

Testing. The size and geometry of our DCB specimens are shown in Figure 1. A very sharp starter crack was introduced by inserting a sheet of aluminum foil between the center laminate of the composite. The specimens were loaded at a crosshead speed of 2 mm/min using an Instron model 4204 through the copper hinge glued to the specimen. The fracture toughness of the specimen was estimated by the critical strain energy release rate. At the point of crack initiation or arrest, this value is known as the critical strain energy release rate, G_{lc} [11].

$$G_{lc} = (P_c^2/2B)(\partial C/\partial a) \quad (1)$$

where P , B , C and a are the applied load, the specimen width, compliance and crack length, respectively. From the load-displacement curves, the compliance, C , can be obtained and plotted against the crack length, a . Using the values of $\partial C/\partial a$ obtained from the compliance-crack growth ($C-a$) curve, G_{lc} can be calculated using equation (1). The relationship between C and a was approximated by:

$$C(a) = R a^n \quad (2)$$

where R and n are constants which are experimentally determined. From Equations 1 and 2, the critical strain energy release rate is given by:

$$G_{lc} = (n P_c^2 C(a) / 2B a) \quad (3)$$

where P_c is the load measured at the point where the crack initiates or reinitiates.

RESULTS AND DISCUSSION

The compliance, C , was calculated from the load-displacement curve and plotted against the crack length. Figure 2(a) and 2(b) shows the typical $C-a$ curves in double logarithmic plot which are based on either the point of *crack initiation* or *crack arrest*. These relationships can be approximated by equation (2). For both crack initiation and arrest, the values of n increase from untreated < ABS < APS treated composites. With the use of the calculated n values in equation 3, the critical strain energy release rate is obtained. In the case of unstable crack growth, the values of G_{lc} may be calculated at the point of crack initiation, reinitiation (propagation) and crack arrest.

Shown in Figures 3(a-c) are the critical strain energy release rates of the three types of composites as a function of the crack length. G_{lc} values were calculated at the point where the crack

initiated or reinitiated. The values of G_{lc} of the untreated composites were approximately independent of the crack length as shown in Figure 3(a). In contrast, the values of G_{lc} for ABS and APS treated composites are more dependent on the crack length. In the range of small crack length, G_{lc} of the ABS-treated composites is almost equal to that of the untreated composite. But, when the crack length above 50 mm, higher G_{lc} values were obtained for ABS treated composites. This was probably due to increased probability of fiber bridging or fiber breakage in the propagating region over that the initiation region of the crack. Increased G_{lc} 's were also found in APS-treated composites with increasing crack length. The value for APS treated material was the highest measured for all three samples.

The values of G_{lc} for the untreated-glass composite calculated at point of arrest was approximately independent of crack length. The G_{lc} value of the ABS treated composite was intermediate between untreated and APS treated composite. G_{lc} values for APS treated composite calculated at the point of arrest was shown to increase with crack length. The averaged G_{lc} values obtained at the point of crack initiation (reinitiation) and arrest were shown in Table 1.

CONCLUSIONS

A fracture toughness test using a DCB specimen can provide a sensitive technique by which effects such as the relative mobility of interfacial species can be probed. The interlamine fracture toughness of glass fiber fabric epoxy composites is influenced by the type of silane coupling agent used. Untreated composites have the lowest critical energy release rate resulting from a poor interface between fiber fabrics and resin. The poor interfacial properties will result in a delamination between the resin and fibers. The ABS treated composites show improvement because of the interfacial layer. They have higher critical energy release rates than the untreated system. The APS treated composite has the highest critical energy release rate which means crack growth through the interface between fiber and resin can effectively transfer the load through the bonding of coupling agent between fibers and resins to the fibers. We believe that this is probably due to the shorter alkyl chain length of the APS which results in a less mobile material than ABS at the coupling agent/epoxy interface. This provides a better graded interface than when ABS is used. Consideration of the mobility

of the coupling agent layer should allow the most effective choice of an appropriate interfacial system for coupling agent applications.

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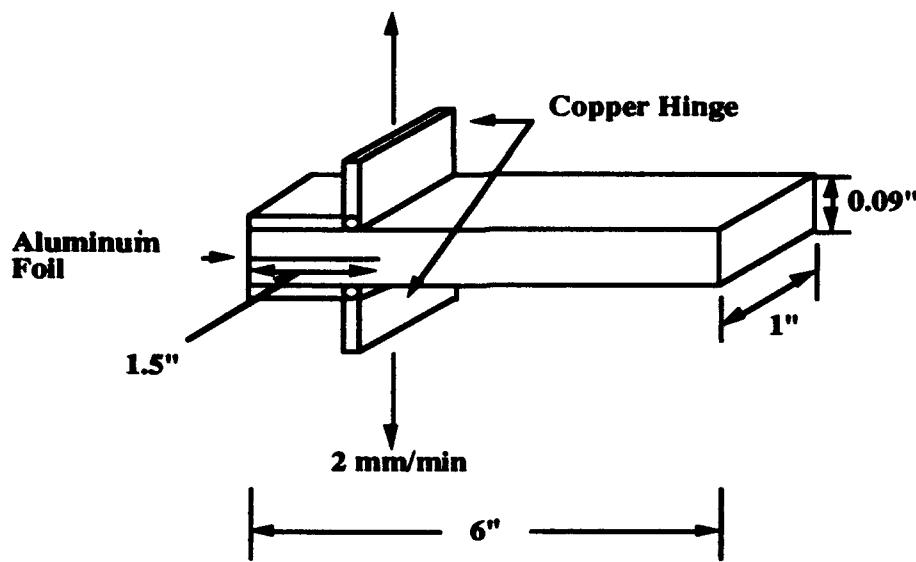


Figure 1. Geometry of the double cantilever beam (DCB) specimen used for the measurement of interlaminar fracture toughness

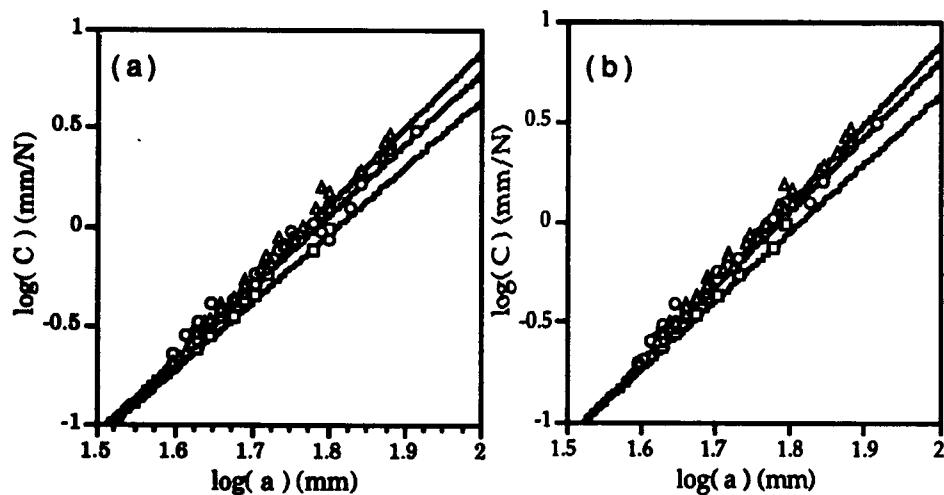


Figure 2. Double logarithmic plot of the typical C-a relations of the composites based on the point of (a) crack initiation (b) crack arrest. Bulk (s), 2% ABS (o), 2% APS (Δ).

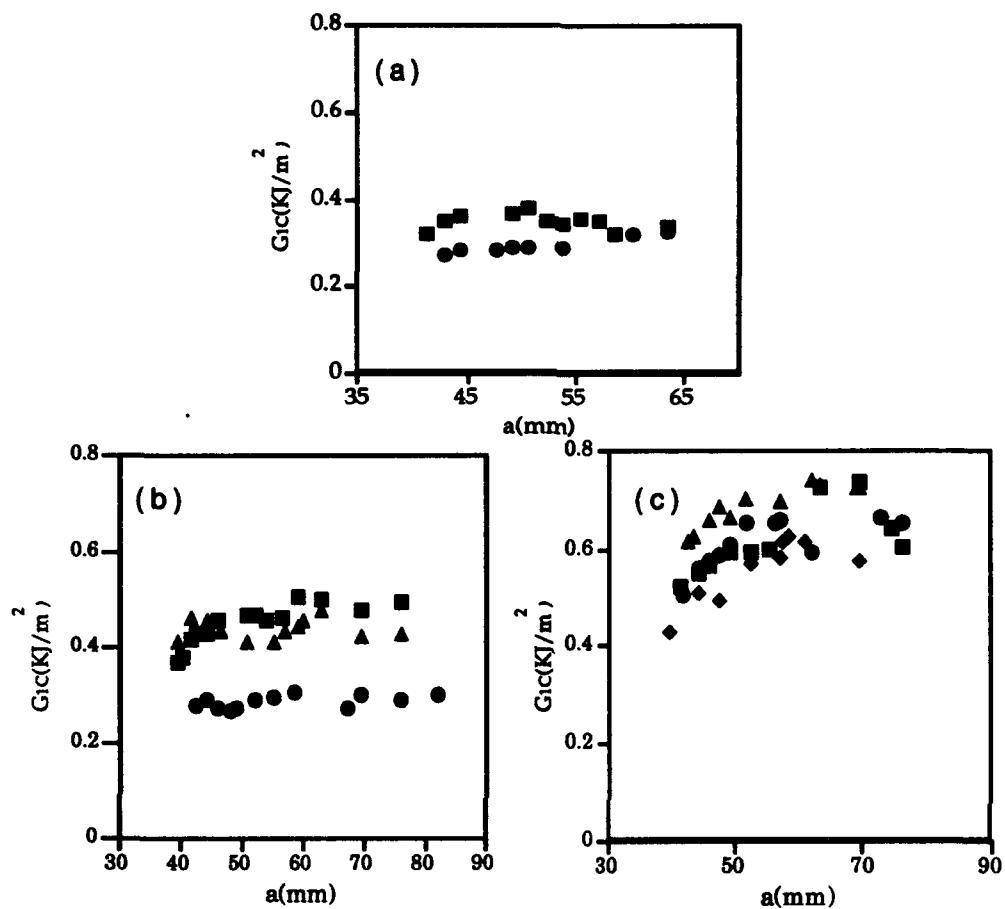


Figure 3(a-c). Critical energy release rate, G_{1c} , of the composites as a function of crack length based on point of initiation. (a) untreated (b) ABS from 2% solution (c) APS from 2% solution.

Table I. The slopes of compliance-crack growth plots (n) and average critical energy release rate (G_{1c}) based on crack initiation (superscript i) and crack arrest (superscript a).

	n^i	n^a	$G_{1c}^i(\text{KJ/m}^2)$	$G_{1c}^a(\text{KJ/m}^2)$
Bulk	3.45	3.44	0.31 ± 0.02	0.32 ± 0.03
2ABS	3.78	3.70	0.37 ± 0.10	0.39 ± 0.11
2APS	3.97	3.92	0.59 ± 0.05	0.61 ± 0.051